REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	September 6, 1995	Reprint

4. TITLE AND SUBTITLE
Convergence Acceleration for the Kohn Variational Method in the presence of a long-range interaction

5. FUNDING NUMBERS
PR 2303
TA GD
WU 06

6. AUTHOR(S)
Robert C. Forrey*
Robert Nyden Hill**
Ramesh D. Sharma

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Phillips Laboratory/GPOS
29 Randolph Road
Hanscom AFB, MA 01731-3010

8. PERFORMING ORGANIZATION REPORT NUMBER
PL-TR-95-2119

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

* Harvard-Smithsonian Ctr for Astrophysics; ** University of Delaware, Dept of Physics & Astronomy
Reprinted from Preprint Series, No. 4154, Harvard-Smithsonian Ctr for Astrophysics
(To appear in Physical Review A 1 Oct 1995)

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release: distribution unlimited

12b. DISTRIBUTION CODE

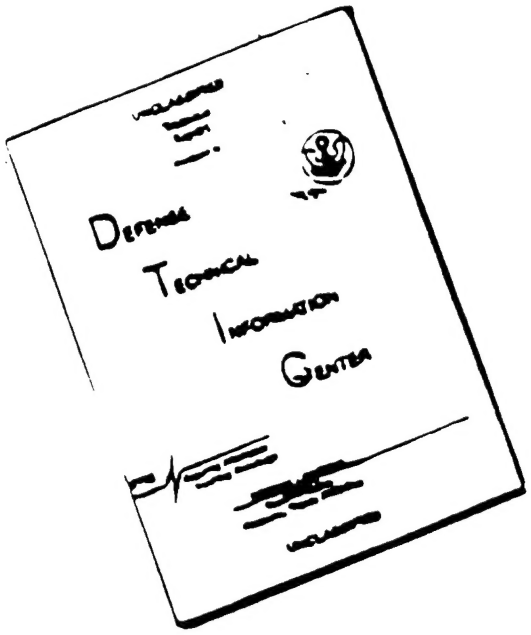
13. ABSTRACT (Maximum 200 words)

The paper presents a distorted wave generalization of the S-matrix version of the Kohn variational principal developed by Zhang, Chu, and Miller [J. Chem. Phys. 88, 10 (1988)]. For scattering in the presence of a long range interaction, the large-r asymptotic solution to the Schrodinger equation is built into the Kohn variational principal order by order in an effort to accelerate convergence of the short-range square integrable part of the basis set expansion. The improvement in the rate of convergence is demonstarated by applying the method to a long-range model potential. Multichannel scattering is discussed.

14. SUBJECT TERMS	15. NUMBER OF PAGES
Scattering Matrix, Kohn Variational Method, Schrodinger Equation, Long range interaction, Multichannel scattering	31
	16. PRICE CODE

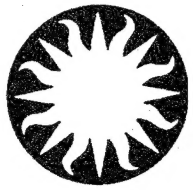
17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	SAR

DISCLAIMER NOTICE



THIS DOCUMENT IS BEST QUALITY AVAILABLE. THE COPY FURNISHED TO DTIC CONTAINED A SIGNIFICANT NUMBER OF PAGES WHICH DO NOT REPRODUCE LEGIBLY.

Harvard-Smithsonian Center for Astrophysics



Preprint Series

No. 4154
(Received August 16, 1995)

CONVERGENCE ACCELERATION FOR THE KOHN VARIATIONAL METHOD IN THE PRESENCE OF A LONG-RANGE INTERACTION

Robert C. Forrey
Harvard-Smithsonian Center for Astrophysics

Robert Nyden Hill
Department of Physics and Astronomy, University of Delaware

and

Ramesh D. Sharma
Phillips Laboratory (GPOS), Hanscom Air Force Base

To appear in
Physical Review A
October 1, 1995

HARVARD COLLEGE OBSERVATORY SMITHSONIAN ASTROPHYSICAL OBSERVATORY
60 Garden Street, Cambridge, Massachusetts 02138

Center for Astrophysics
Preprint Series No. 4154

Convergence acceleration for the Kohn variational method in the presence of a long–range interaction

Robert C. Forrey

Harvard–Smithsonian Center for Astrophysics,

60 Garden Street, Cambridge MA 02138

Robert Nyden Hill

Department of Physics and Astronomy,

University of Delaware, Newark, Delaware 19716

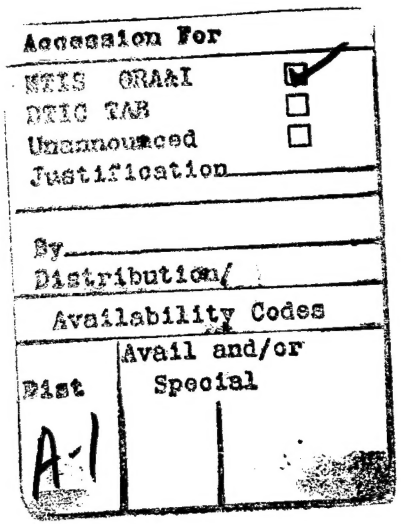
Ramesh D. Sharma

Phillips Laboratory (GPOS),

Hanscom Air Force Base, MA 01731

Abstract

This paper presents a distorted wave generalization of the S–matrix version of the Kohn variational principle developed by Zhang, Chu, and Miller [J. Chem. Phys. **88** 10, (1988)]. For scattering in the presence of a long–range interaction, the large–r asymptotic solution to the Schrödinger equation is built into the Kohn variational principle order by order in an effort to accelerate the convergence of the short–range square integrable part of the basis set expansion. The improvement in the rate of convergence is demonstrated by applying the method to a long–range model potential. Multichannel scattering is discussed.



1 Introduction

Recent interest in low–energy scattering [1] in the presence of a long–range interaction has motivated the development of new methods for computing phase shifts [2]–[4] through use of asymptotic effective range expansions [5]. The present study, while applicable in the zero–energy limit, is motivated by the desire to calculate phase shifts when the energy is too high to apply effective range formulas, but too low to use perturbative expansions. The method, which is a distorted wave generalization of the complex Kohn variational principle developed by Zhang, Chu, and Miller [6], is applied to single channel potential scattering. The eventual objective is the construction of rapidly convergent approximations to scattering wave functions in the multichannel case where standard propagation algorithms are no longer effective. The basic idea is to incorporate the large–r asymptotic solution to the Schrödinger equation into the Kohn variational principle in such a way that the convergence of the short–range square integrable (L^2) part of the basis set expansion is accelerated. The present work shows that the large–r asymptotic behavior can be systematically incorporated to arbitrarily high order by adding well–behaved 'convergence acceleration functions' to the basis set. Plane waves and Coulomb waves are used as examples to show the

order by order improvement in the convergence rate of the L^2 basis set. In order to further demonstrate the acceleration procedure, the method is applied to a model potential that falls off as r^{-4} at large distances, which is a case that arises in charged particle scattering by a neutral polarizable target. The paper concludes with a brief discussion of the application of the convergence acceleration procedure to multichannel scattering.

2 Distorted Wave Theory

This section develops a distorted wave approach to potential scattering in the presence of a long–range interaction. Interaction potentials that fall off as an inverse power of r at large distances from the scattering center are considered. The analysis begins with the partial wave Schrödinger equation

$$\left[\frac{d^2}{dr^2} + k^2 - U(r) - \frac{\ell(\ell+1)}{r^2}\right] u_\ell(r) = 0, \tag{2.1}$$

and assumes that the long–range part of the potential has the form

$$U(r) = \frac{2\mu}{\hbar^2} V(r) \sim \sum_{\lambda=1}^{\infty} a_\lambda \, r^{-\lambda}, \qquad r \to \infty \ . \tag{2.2}$$

A formal partial wave solution $u_\ell(r)$ can be constructed by looking for a large r expansion of the form

$$u_\ell(r) \;\sim\; -\exp(-ikr)\sum_{n=0}^{\infty} f_{\ell,n}^{(-)}\, r^{-n+i\nu} + S_\ell \exp(+ikr)\sum_{n=0}^{\infty} f_{\ell,n}^{(+)}\, r^{-n-i\nu}\,. \tag{2.3}$$

The Coulomb phase parameter

$$\nu = \frac{a_1}{2k} \tag{2.4}$$

is necessary when $a_1 \neq 0$. The asymptotic expansion coefficients $f_{\ell,n}^{(\pm)}$ for $n > 0$ provide a distorted wave generalization of the standard method for short–range potentials, which includes only the $n = 0$ term of the expansion (2.3) in the basis set. Putting (2.3) into (2.1) and equating coefficients of like powers of r yields the recursion relation

$$\begin{aligned}&[a_1 \pm 2ik(n \pm i\nu + 1)]\; f_{\ell,n+1}^{(\pm)} + \sum_{\lambda=0}^{n} a_{\lambda+2}\; f_{\ell,n-\lambda}^{(\pm)} \\ &\quad + \;\; [\ell(\ell+1) - (n \pm i\nu)(n \pm i\nu + 1)]\; f_{\ell,n}^{(\pm)} = 0\end{aligned} \tag{2.5}$$

for the distortion coefficients $f_{\ell,n}^{(\pm)}$. The zeroth–order coefficients

$$f_{\ell,0}^{(\pm)} = (\hbar k/\mu)^{-1/2} \exp[i(\sigma_\ell^{(\pm)} \mp \pi\ell/2 \mp \nu \ln 2k)], \tag{2.6}$$

where

$$\sigma_\ell^{(\pm)} = \arg\left[\Gamma(\ell + 1 \pm i\nu)\right], \tag{2.7}$$

have been chosen to be consistent with the normalization convention used by Zhang, Chu, and Miller [6]. The higher order coefficients are determined from (2.5). The first two are

$$f_{\ell,1}^{(\pm)} = \left(\frac{\pm i}{2k}\right)[a_2 + \ell(\ell+1) \mp i\nu(1 \pm i\nu)]\; f_{\ell,0}^{(\pm)}, \tag{2.8}$$

and

$$f_{\ell,2}^{(\pm)} \;=\; \left(\frac{\pm i}{4k}\right)\left\{[a_2 + \ell(\ell+1) - (1 \pm i\nu)(2 \pm i\nu)]\; f_{\ell,1}^{(\pm)} + a_3\, f_{\ell,0}^{(\pm)}\right\}. \tag{2.9}$$

The next step incorporates the large r asymptotic behavior deduced above into the basis set. A basis function (or functions) is sought that (1) has a large r asymptotic expansion whose first N terms agree with the exact large r expansion (2.3), (2) remains well–behaved when r is small, (3) does not have spurious singularities which slow down the convergence, and (4) leads to tractable matrix element integrals. One possible choice uses the incomplete gamma function

$$\gamma(n+\ell+1\pm i\nu,\alpha r) = \frac{(\alpha r)^{n+\ell+1\pm i\nu}}{(n+\ell+1\pm i\nu)}$$
$$\times \ {}_1F_1(n+\ell+1\pm i\nu, n+\ell+2\pm i\nu, -\alpha r) \qquad (2.10)$$

as a 'cutoff function,' where α is an arbitrary non–linear variational parameter. The functions

$$h_\ell^{(\pm)}(r) = \sum_{n=0}^{N} f_{\ell,n}^{(\pm)}\, g_{\ell,n}^{(\pm)}(r), \qquad (2.11)$$

where

$$g_{\ell,n}^{(\pm)}(r) = \frac{\gamma(n+\ell+1\pm i\nu,\alpha r)}{\Gamma(n+\ell+1\pm i\nu)}\,\frac{\exp(\pm ikr)}{r^{n\pm i\nu}}, \qquad (2.12)$$

are added to the basis. The large r asymptotic formula

$$\gamma(n+\ell+1\pm i\nu,\alpha r) = \Gamma(n+\ell+1\pm i\nu) + O\left[(-\alpha r)^{n+\ell\pm i\nu}\exp(-\alpha r)\right] \qquad (2.13)$$

can be used to show that the combination $-h_\ell^{(-)}(r) + S_\ell\, h_\ell^{(+)}(r)$ has a large r asymptotic expansion whose first N terms agree with (2.3). The small r convergent expansion

$$\gamma(n+\ell+1\pm i\nu,\alpha r) = \sum_{k=0}^{\infty}\frac{(-1)^k\,(\alpha r)^{n+\ell+1\pm i\nu+k}}{k!\,(n+\ell+1\pm i\nu+k)} \qquad (2.14)$$

can be used to show that the functions $h_\ell^{(\pm)}(r)$ are analytic functions of r at $r = 0$. When the Coulomb parameter ν is zero, the cutoff function (2.10) simplifies to

$$\gamma(n+\ell+1,\alpha r) \ = \ (n+\ell)!\left[1-\exp(-\alpha r)\sum_{m=0}^{n+\ell}\frac{(\alpha r)^m}{m!}\right]. \qquad (2.15)$$

This reduces to the cutoff function used by Zhang, Chu, and Miller when $n = \ell = 0$. Matrix element evaluation is particularly simple when the cutoff function takes the form (2.15).

The distorted wave theory presented here differs from more standard treatments (see, for example, [7]) that require matrix elements of the short–range part of the potential taken between states that are distorted by the long–range part of the potential. The present approach should be more efficient if the large–r expansion of the distorted waves used to calculate matrix elements of the short–range part of the potential in standard treatments does not agree with the exact large r expansion (2.3). In the more general case of multichannel scattering, the distortion coefficients $f_{\ell,n}^{(\pm)}$ are still determined

from the Schrödinger equation as above, but will depend on the internal coordinates of the target.

3 Rate of Convergence Theory

This section provides a brief overview of a theory of convergence rates for Laguerre polynomial expansions. The theory has been rigorously applied to bound states [8] and contains many features that should also be applicable to scattering states. The analysis begins with the formal expansion

$$u_\ell(r) \;=\; \sum_{m=0}^{\infty} c_{\ell,m}\,\phi_{\ell,m}(r) \tag{3.1}$$

of the partial wave solution $u_\ell(r)$ in the basis

$$\phi_{\ell,m}(r) \;=\; (ar)^{\ell+1}\exp(-ar/2)L_m^{(\lambda)}(ar), \tag{3.2}$$

where the Laguerre polynomials $L_m^{(\lambda)}$ are defined by the generating function

$$(1-z)^{-\lambda-1}\exp\left[-\left(\frac{xz}{1-z}\right)\right] \;=\; \sum_{m=0}^{\infty} L_m^{(\lambda)}(x)\;z^m\,, \tag{3.3}$$

and the coefficients $c_{\ell,m}$ are given by the integral

$$c_{\ell,m} = \frac{m!\,a}{\Gamma(m+\lambda+1)}\int_0^\infty \phi_{\ell,m}(r)u_\ell(r)(ar)^{\lambda-2\ell-2}\,dr. \tag{3.4}$$

The functions $\phi_{\ell,m}$, which are called Sturmians, have been chosen for their excellent numerical stability properties as the number of basis functions is increased. Application of the theory to other basis sets built from classical orthogonal polynomials (see [9] for bound states) should be similar to the discussion presented here.

The expansion (3.1) cannot converge in L^2 because $u_\ell(r)$ is not square integrable. The coefficients $c_{\ell,m}$ are nevertheless well defined because the integral (3.4) is convergent. The expansion (3.1) provides a discrete L^2 representation of the continuum [10]. In some cases, a pure Coulomb potential for example, the L^2 representation can be shown [11] to possess conditional pointwise convergence that is very slow. In practice, however, we would like to have an expansion which is rapidly convergent in L^2.

This goal can be achieved by using the modified expansion

$$u_\ell(r) \;=\; -h_\ell^{(-)}(r) + \tilde{S}_\ell\; h_\ell^{(+)}(r) + \sum_{m=0}^{\infty} \tilde{c}_{\ell,m}\,\phi_{\ell,m}(r) \tag{3.5}$$

where the 'convergence acceleration functions' $h_\ell^{(\pm)}(r)$ in (3.5) have the prop-

erty that the coefficients of the formal expansion

$$h_\ell^{(\pm)}(r) \;=\; \sum_{m=0}^{\infty} c_{\ell,m}^{(\pm)}\, \phi_{\ell,m}(r) \tag{3.6}$$

obey the condition

$$c_{\ell,m} \;\approx\; -c_{\ell,m}^{(-)} + \tilde{S}_\ell\, c_{\ell,m}^{(+)} \tag{3.7}$$

for m large. The coefficients

$$\tilde{c}_{\ell,m} \;=\; c_{\ell,m} + c_{\ell,m}^{(-)} - \tilde{S}_\ell\, c_{\ell,m}^{(+)} \tag{3.8}$$

will then decrease fast enough for large m to make the sum over m in (3.5) rapidly convergent in L^2. The functions (3.6) are reminiscent of the L^2 approach to scattering developed by Heller and Yamani [12]. In the present case, however, the L^2 expansions (3.1) and (3.6) are used only as a formal tool to understand the convergence rate of the Sturmian part of (3.5). It will be shown that the condition (3.7) can be met by using the acceleration functions (2.11) introduced in the distorted wave theory of the previous section. The functions (2.11) for $N = 0$ are normally used as the starting point for discussions of the Kohn variational principle. In the present case,

however, the acceleration functions are actually a consequence of a general rate of convergence theory, and the effect that increasing N will have on the convergence rate can be analyzed. In order to understand the convergence rate of the Sturmian basis set, it is necessary to determine the large–m behavior of the expansion coefficients $c_{\ell,m}$ and $c_{\ell,m}^{(\pm)}$. The analysis for the $c_{\ell,m}^{(\pm)}$ will be presented first. Following [13], define a generating function

$$g_\ell^{(\pm)}(z) \;=\; \sum_{m=0}^{\infty} I_{\ell,m}^{(\pm)}\, z^m \;, \tag{3.9}$$

where

$$c_{\ell,m}^{(\pm)} = a^{\lambda-\ell} \frac{m!}{(m+\lambda)!}\, I_{\ell,m}^{(\pm)} \;. \tag{3.10}$$

The large–m behavior of $c_{\ell,m}^{(\pm)}$, and therefore the rate of convergence of the Sturmian expansion, is controlled by the singularities of $g_\ell^{(\pm)}(z)$ closest to the origin in the complex–z plane [13]. Equations (3.2), (3.3), (3.6), and the orthogonality relation for the Laguerre polynomials can be used to obtain an explicit formula for the generating function $g_\ell^{(\pm)}(z)$. The result is

$$g_\ell^{(\pm)}(z) \;=\; (1-z)^{-\lambda-1}\, H_\ell^{(\pm)}(s) \tag{3.11}$$

where $H_\ell^{(\pm)}(s)$ is the Laplace transform

$$H_\ell^{(\pm)}(s) \;=\; \int_0^\infty r^{\lambda-\ell-1} h_\ell^{(\pm)}(r) \exp(-sr) dr \qquad (3.12)$$

and

$$s = \frac{a(1+z)}{2(1-z)} \; . \qquad (3.13)$$

Using (2.11) and (3.12) yields

$$H_\ell^{(\pm)}(s) \;=\; \lambda! \sum_{n=0}^{N} \frac{\alpha^{n+\ell+1\pm i\nu}}{\Gamma(n+\ell+2\pm i\nu)} \, f_{\ell,n}^{(\pm)} \, F_{\ell,n}^{(\pm)}(s) \qquad (3.14)$$

where

$$F_{\ell,n}^{(\pm)}(s) = (s \mp ik)^{-(\lambda+1)}$$
$$\times \;\; {}_2F_1(\lambda+1, n+\ell+1\pm i\nu, n+\ell+2\pm i\nu; \frac{-\alpha}{s\mp ik}) \; . \qquad (3.15)$$

The hypergeometric function ${}_2F_1(a,b;c,\zeta)$ is an analytic function of ζ except for singularities at $\zeta = 1$ and $\zeta = \infty$. It follows that the $H_\ell^{(\pm)}(s)$ are analytic functions of s except for singularities at $s = \pm ik$ and $s = -\alpha \pm ik$.

The singularities at $s = \pm ik$ are the physical singularities from the large r behavior of the partial wave solution $u_\ell(r)$ which we are trying to model. The singularities at $s = -\alpha \pm ik$ are spurious singularities which come from the $(-\alpha r)^{n+\ell\pm i\nu} \exp(-\alpha r)$ piece in the large r behavior of the cutoff function [see equation (2.13)]. If the scale factor a in (3.13) is chosen to be equal to twice the value of the non–linear variational parameter α in (2.12), then the spurious singularities will be located in the complex z–plane at

$$z = 1 \pm i\left(\frac{2\alpha}{k}\right) \; , \qquad (3.16)$$

and with an appropriate choice of α can be pushed far enough away from the origin so that they do not affect the convergence rate. The physical singularities that we are trying to cancel will then control the convergence rate. These singularities are located on the unit circle in the complex z–plane at

$$z = z_0^{\pm} = -\left(\frac{\alpha \mp ik}{\alpha \pm ik}\right) \; . \qquad (3.17)$$

The transformation theory of the hypergeometric series can be used to show that the expansions of the $H_\ell^{(\pm)}(s)$ about the singularities (3.17) have the

form

$$H_\ell^{(\pm)}(s) = \sum_{n=0}^{N} f_{\ell,n}^{(\pm)} \frac{\Gamma(\lambda \mp i\nu - n - \ell)}{(s \mp ik)^{\lambda - n - \ell \mp i\nu}} + \left\{ \begin{array}{c} \text{analytic} \\ \text{function} \end{array} \right\}. \quad (3.18)$$

The expansions of the generating functions about the singular points $z_0^{\pm}$ can be derived from (3.18). They are

$$g_\ell^{(\pm)}(z) = \sum_{n=0}^{\infty} A_{\ell,n}^{(\pm)} \, (z - z_0^{\pm})^{\sigma+n} \quad (3.19)$$

where

$$A_{\ell,n}^{(\pm)} = \sum_{m=0}^{n} f_{\ell,n-m}^{(\pm)} \, \Gamma(m - n - \sigma) \begin{pmatrix} n+\sigma+\lambda \\ m \end{pmatrix} \left[\frac{(\alpha \pm ik)^{\sigma+n-m}}{(1 - z_0^{\pm})^{\sigma+\lambda+n+1}} \right] \quad (3.20)$$

with $\sigma = \ell - \lambda \pm i\nu$. The method of Darboux (see [13], [14] pp. 532-535, [15] pp. 116-122 and 145-146, [16] pp. 309-315 and 321) can be used in combination with the asymptotic formula

$$\begin{pmatrix} \sigma+n \\ m \end{pmatrix} = \frac{(-1)^m}{\Gamma(-\sigma-n)} m^{-\sigma-n-1} \left[1 + O\left(m^{-1}\right) \right] \quad (3.21)$$

for binomial coefficients to deduce the asymptotic estimate

$$I_{\ell,m}^{(\pm)} = \sum_{n=0}^{N} A_{\ell,n}^{(\pm)} \begin{pmatrix} \sigma+n \\ m \end{pmatrix} \left(-z_0^{\pm}\right)^{\sigma+n-m} + O\left(m^{-\sigma-N-2}\right) . \quad (3.22)$$

The asymptotic $c_{\ell,m}^{(\pm)}$ are found from (3.10) and (3.22).

The large m asymptotic analysis of the $c_{\ell,m}$ is similar. The Laplace transform $H_\ell^{(\pm)}(s)$ introduced in (3.12) is replaced by

$$U_\ell(s) = \int_0^{\infty} r^{\lambda-\ell-1} u_\ell(r) \exp(-sr) dr \quad (3.23)$$

Because the $u_\ell(r)$ are not known explicitly, the behavior of $U_\ell(s)$ in the neighborhood of the points $s = \pm ik$ cannot be deduced by invoking properties of known, well studied functions, and theorems on the asymptotics of the Laplace transform must be used (see [15] Theorem 13, p. 322 or [17] Example 4.6.1 p. 134). The needed result, which follows from the large r expansion (2.3) as a consequence of these theorems, is

$$U_\ell(s) = U_\ell^{(\pm)}(s) + \left\{ \begin{array}{c} \text{analytic} \\ \text{function} \end{array} \right\} \quad (3.24)$$

where

$$U_\ell^{(-)}(s) \sim -\sum_{n=0}^{\infty} f_{\ell,n}^{(-)} \frac{\Gamma(\lambda - i\nu - n - \ell)}{(s - ik)^{\lambda - n - \ell - i\nu}}, \tag{3.25}$$

$$U_\ell^{(+)}(s) \sim S_\ell \sum_{n=0}^{\infty} f_{\ell,n}^{(+)} \frac{\Gamma(\lambda + i\nu - n - \ell)}{(s + ik)^{\lambda - n - \ell + i\nu}}. \tag{3.26}$$

The rest of the analysis goes through as for the $c_{\ell,m}^{(\pm)}$. The result is

$$c_{\ell,m} = a^{\lambda-\ell} \frac{m!}{(m+\lambda)!} I_{\ell,m} , \tag{3.27}$$

where

$$\begin{aligned} I_{\ell,m} \sim \sum_{n=0}^{\infty} \Bigg[& - A_{\ell,n}^{(-)} \binom{\ell - \lambda - i\nu + n}{m} \left(-z_0^-\right)^{\ell-\lambda-i\nu+n-m} \\ & + S_\ell \, A_{\ell,n}^{(+)} \binom{\ell - \lambda + i\nu + n}{m} \left(-z_0^+\right)^{\ell-\lambda+i\nu+n-m} \Bigg]. \end{aligned} \tag{3.28}$$

Equation (3.21) shows that each term of the asymptotic expansion (3.28) is smaller than the preceding term by a factor of m^{-1}. It follows from (3.8), (3.22), and (3.28) that

$$\tilde{c}_{\ell,m} = O\left(m^{-\ell-N-2}\right) \tag{3.29}$$

for m large if $\tilde{S}_\ell = S_\ell$. In an actual calculation, of course, $\tilde{S}_\ell$ will differ slightly from S_ℓ, but the variational principle will ensure that the error which arises from this difference is of the same order as the error which comes from truncating the expansion in (3.5). Section 5 contains a numerical demonstration that the asymptotic expansion (3.22) agrees well with the exact coefficients for both plane and Coulomb waves, thus confirming the hypothesis that the condition (3.7) can be met by using the acceleration functions (2.11).

Equation (3.29) shows that the asymptotic behavior of the coefficients $\tilde{c}_{\ell,m}$ is improved by a factor of m^{-1} when N is increased by 1. Therefore, we expect that an increase in the order N of the $h_{\ell,m}^{(\pm)}$ defined in (2.11) will lead to a decrease in the number of Sturmian functions $\phi_{\ell,m}$ needed in (3.5). The advantage is that we know the values of the distortion coefficients $f_{\ell,n}^{(\pm)}$, but the unknown coefficents $\tilde{c}_{\ell,m}$ need to be determined variationally. A second advantage is that by solving the large r part of the problem exactly, a more uniform pattern of convergence is obtained. This is especially appealing for an unbounded variational principle, such as the Kohn principle, since it is often difficult to determine the stationary points that yield the approximations to the solutions which the trial function is attempting to model. A third advantage is that a single non-linear parameter is used to describe the full configuration space. This is possible because the Sturmian basis does

not need to handle the large r part of the wave function since it is already put in by the convergence acceleration functions.

4 Variational Method

The following notational changes will be made in order to simplify the discussion: the ℓ–dependence of each partial wave is suppressed, and $p, q = \{0, 1\}$ is used to designate the respective incoming and outgoing solutions. The variational S–matrix element is then given by [6]

$$\tilde{S} = \frac{i}{\hbar}(B - C^2/D) \tag{4.1}$$

where

$$B = M_{00} - M_0^T \cdot M^{-1} \cdot M_0 \tag{4.2}$$

$$C = M_{10} - M_1^T \cdot M^{-1} \cdot M_0 \tag{4.3}$$

and

$$D = B^* \;=\; M_{11} - M_1^T \cdot M^{-1} \cdot M_1 \; . \tag{4.4}$$

As is emphasized in [6], the symmetry between the incoming function $h_\ell^{(-)}$ and the outgoing function $h_\ell^{(+)}$ allows the number of individual matrix elements that need to be computed to be minimized. These matrix elements are defined by

$$M_{pq} = < h^{(p)}|H - E|h^{(q)} > \tag{4.5}$$

$$(M_q)_m = < \phi_m|H - E|h^{(q)} > \tag{4.6}$$

and

$$(M)_{mn} \;=\; < \phi_m|H - E|\phi_n > \; . \tag{4.7}$$

Equations (2.11), (4.5), and (4.6) can be used to show that

$$M_{pq} \;=\; \sum_{m=0}^{N} \sum_{n=0}^{N} f_m^{(p)} f_n^{(q)} < g_m^{(p)}|H - E|g_n^{(q)} > \tag{4.8}$$

and

$$(M_q)_m = \sum_{n=0}^{N} f_n^{(q)} < \phi_m | H - E | g_n^{(q)} > \ . \tag{4.9}$$

For multichannel scattering, the individual matrix elements (4.5–4.7) become matrices with respect to the internal quantum numbers, and the distortion coefficients $f_{\ell,n}^{(\pm)}$ become functions of all the internal coordinates as well as the projectile angular variables. This differs from the distorted wave approach suggested by Zhang and Miller [18] which requires a multichannel distortion potential that introduces modifications to the basic formulas (4.5) and (4.6). In the present approach, instead of dealing with distortion potentials that are normally numerical functions of the channel radial coordinate r, we have analytic functions in the full configuration space which are exact solutions to the large–r Schrödinger equation for each channel. These analytic functions have the advantage that they allow for transformations to coordinate systems that are better suited for describing the composite system in the interaction region.

5 Numerical Results

This section provides numerical illustrations of the convergence acceleration process. Exact expansion coefficients $c_{\ell,m}$ for spherical Bessel functions and

Coulomb wave functions are compared with large m asymptotic formulas. The convergence acceleration process is then applied to a simple potential scattering problem.

Consider first the expansion coefficients $c_{\ell,m}$ defined by (3.4) when $u_\ell(r)$ is the Coulomb wave function

$$u_\ell(r) = r^{\ell+1} \exp(ikr)\ {}_1F_1(\ell+1+i\nu, 2\ell+2, -2ikr), \tag{5.1}$$

which reduces to a spherical Bessel function when $\nu = 0$. The exact coefficients $c_{\ell,m}$ can be obtained from the Laplace transform

$$\begin{aligned} U_\ell(s) &= \int_0^\infty r^{\lambda-\ell-1} u_\ell(r) \exp(-sr) dr \\ &= \frac{\lambda!}{(s-ik)^{\lambda+1}}\ {}_2F_1(\lambda+1, \ell+1+i\nu, 2\ell+2, \frac{-2ik}{s-ik})\ . \end{aligned} \tag{5.2}$$

For $\lambda = 2l+1$, it is easy to show that

$$U_\ell(s) = \frac{(2l+1)!}{(s^2+k^2)^{\ell+1}} \left(\frac{s-ik}{s+ik}\right)^{i\nu}, \tag{5.3}$$

which leads to

$$c_{\ell,m} = \frac{m!\,(2l+1)!\,(2\alpha)^{\ell+1}}{(m+2\ell+1)!\,(\alpha^2+k^2)^{\ell+1}} \left(\frac{\alpha-ik}{\alpha+ik}\right)^{i\nu}$$

$$\times \sum_{n=0}^{m} \begin{pmatrix} m-n+l-i\nu \\ m-n \end{pmatrix} \begin{pmatrix} n+l+i\nu \\ n \end{pmatrix} (z_0^+)^{n-m} (z_0^-)^{-n} \ . \quad (5.4)$$

Table 1 compares the asymptotic coefficients (3.7) with the exact coefficients (5.4) for the plane wave case when $\nu = 0$. For $m \geq 5$, the difference between the asymptotic and exact coefficients decreases as N increases, indicating that the long–range centrifugal potential is controlling the convergence rate of the Sturmian expansion. When $N = \ell$, the recursion relation (2.5) terminates and the L^2 basis set converges exponentially fast. Table 2 shows the same comparison for the Coulomb case when $\nu = 1/2k$. In this case, the recursion relation never terminates, so the L^2 basis set will never converge exponentially. However, we see from Table 2 that the convergence rate can be significantly improved by going to high values of N.

In practice, if the long–range coefficients a_λ in (2.2) are zero for $\lambda > 1$, then it would be more efficient to use the incoming and outgoing Coulomb functions (or spherical Hankel functions if $\nu = 0$) multiplied by the zeroth–order cutoff function (2.15). The distorted wave formalism of section 2 will thefore be illustrated by an example for which the a_λ are non–zero. Many

theoretical studies [6][19]–[21] have been conducted on the attractive and repulsive exponential potentials

$$V(r) = \pm \exp(-r) \ . \quad (5.5)$$

The present work performs a similar study on a potential that behaves like (5.5) at short distances, but has a long range $r^{-\lambda}$ tail. A simple choice is

$$V(r) = (\pm\lambda)\frac{\gamma(\lambda,r)}{r^\lambda} \quad (5.6)$$

$$= \begin{cases} \pm\exp(-r) & r \to 0 \\ \pm(\lambda!)\, r^{-\lambda} & r \to \infty \end{cases} \quad (5.7)$$

In particular, we choose $\lambda = 4$, a case that arises in charged particle scattering by a neutral polarizable target. Tables 3 and 4 illustrate the kind of improvement in the convergence rate that can be achieved for this potential. The results, which are for $k = .5$ atomic units, indicate that the convergence acceleration procedure usually yields a more accurate phase shift for a given number of basis functions. There are, however, instances where an increase in N causes a decrease in the accuracy of the phase shift. For example, in the $M = 2$, $N = 5$ entry of the top part of Table 3, the relative error looks

anomalously small when compared to its neighboring entries. Since the unitarity of the S–matrix (measured by the imaginary part of the numerical K–matrix) generally improves with increasing M and N, exceptional accuracy for small M and N can usually be regarded as fortuitous. In fact, the unitarity of the S–matrix for the anomolous $M = 2$, $N = 5$ entry is only good to four digits, so at least one of the digits of agreement for the phase shift is actually noise.

6 Conclusions

As emphasized by Zhang and Miller [18], the S–matrix version of the Kohn principle requires mostly energy independent matrix element evaluations, followed by standard linear algebra computations. The exchange interactions which plague coupled channel differential equations are easily handled by the basis sets, and the Kohn anomalies which arise in the K-matrix version of the Kohn principle are easily avoided. In the present work, we emphasize that all of the advantages of the original formulation [6] of the S–matrix version of the Kohn variational method are retained.

The motivation of the present work is to obtain rapid convergence in the general case of multichannel scattering. Since the computational effort for multichannel scattering scales as the square of the product of target and

translational functions, it is highly desirable to keep the number of translational L^2 functions as small as possible. We have shown in the special case of potential scattering how to incorporate long–range distortion into the non–L^2 basis functions in such a way that the size of the L^2 basis set can be reduced. The extension to multichannel scattering should be straight–forward, and is the subject of ongoing research.

7 Acknowledgements

This research was supported in part by AFOSR under task 2303 EP and Phillips Laboratory project 007, by NSF Grants PHY-9106797 and PHY-9406318 to RNH, and by a grant to Alex Dalgarno by the US Department of Energy. The authors acknowledge the generous encouragement and advice of Alex Dalgarno and Dudley Herschbach, and helpful discussions with the researchers at ITAMP where much of the work was conducted.

References

[1] See, for example, R. Cote, A. Dalgarno and M. J. Jamieson, Phys. Rev. A **50**, 399 (1994).

[2] M. Marinescu, Phys. Rev. A **50**, 3177 (1994).

[3] G. F. Gribakin and V. V. Flambaum, Phys. Rev. A **48**, 546 (1993).

[4] M. J. Cavagnero, Phys. Rev. A **50**, 2841 (1994).

[5] T. F. O'Malley, L. Spruch, and L. Rosenberg, J. Math. Phys. **2**, 491 (1961).

[6] J. Z. H. Zhang, S.-I. Chu, and W. H. Miller, J. Chem. Phys. **88**, 6233 (1988).

[7] L. I. Schiff, *Quantum Mechanics*, 3rd ed., McGraw–Hill, New York, (1968).

[8] R. N. Hill, J. Chem. Phys. **83**, 1173 (1985).

[9] R. N. Hill, Phys. Rev. A (in press).

[10] H. A. Yamani and W. P. Reinhardt, Phys. Rev. A **11**, 1144 (1975).

[11] I. Bray and A. T. Stelbovics, Phys. Rev. A **46**, 6995 (1992).

[12] E. J. Heller and H. A. Yamani, Phys. Rev. A **9**, 1201 (1974).

[13] R. C. Forrey and R. N. Hill, Annals of Phys. **226**, 88 (1993).

[14] R. Courant and D. Hilbert, *Methods of Mathematical Physics*, (Interscience, New York, 1953), Vol. 1.

[15] R. Wong, *Asymptotic Approximations of Integrals* (Academic, San Diego, 1989).

[16] F. W. J. Olver, *Asymptotics and Special Functions* (Academic, San Diego, 1974).

[17] N. Bleistein and R. A. Handelsman, *Asymptotic Expansions of Integrals* (Holt, Rinehart, & Winston, New York, 1975; reprinted by Dover, 1986).

[18] J. Z. H. Zhang and W. H. Miller, J. Chem. Phys. **91**, 1528 (1989).

[19] G. Staszewska and D. G. Truhlar, Chem. Phys. Lett. **130**, 341 (1986).

[20] K. Takatsuka, R. R. Lucchese, and V. Mckoy, Phys. Rev. A **24**, 1812 (1981).

[21] C. W. McCurdy, T. N. Rescigno, and B. I. Schneider, Phys. Rev. A **36**, 2061 (1987).

Table 1: Relative error in asymptotic expansion coefficients for plane waves (l=4, k=.5, a=2)

m	$N=0$	$N=1$	$N=2$	$N=3$	$N=4*$
5	1×10^{-0}	7×10^{-1}	2×10^{-1}	3×10^{-2}	8×10^{-16}
10	5×10^{-1}	9×10^{-2}	1×10^{-2}	4×10^{-3}	3×10^{-15}
15	3×10^{-0}	2×10^{-0}	3×10^{-1}	2×10^{-2}	2×10^{-13}
20	4×10^{-1}	5×10^{-2}	2×10^{-4}	4×10^{-4}	1×10^{-13}
25	5×10^{-1}	3×10^{-1}	3×10^{-2}	1×10^{-3}	1×10^{-12}
30	3×10^{-1}	4×10^{-2}	7×10^{-4}	8×10^{-5}	2×10^{-13}
35	9×10^{-2}	6×10^{-2}	7×10^{-3}	2×10^{-4}	2×10^{-12}
40	3×10^{-1}	3×10^{-2}	7×10^{-4}	2×10^{-5}	6×10^{-13}
45	2×10^{-2}	2×10^{-2}	3×10^{-3}	7×10^{-5}	2×10^{-12}
50	3×10^{-1}	2×10^{-2}	7×10^{-4}	6×10^{-6}	2×10^{-12}

*Apparent loss of accuracy is due to the decreasing magnitude of the coefficients as the value of m is increased.

Table 2: Relative error in asymptotic expansion coefficients for Coulomb waves (l=0, k=.5, a=2)

m	$N=0$	$N=1$	$N=2$	$N=3$	$N=4$
5	8×10^{-1}	2×10^{-1}	3×10^{-2}	4×10^{-2}	7×10^{-2}
10	3×10^{-1}	5×10^{-2}	4×10^{-3}	3×10^{-3}	1×10^{-3}
15	2×10^{-1}	3×10^{-2}	4×10^{-3}	4×10^{-4}	2×10^{-4}
20	8×10^{-1}	4×10^{-2}	2×10^{-2}	1×10^{-3}	4×10^{-4}
25	1×10^{-1}	7×10^{-3}	3×10^{-4}	1×10^{-4}	2×10^{-6}
30	8×10^{-2}	7×10^{-3}	4×10^{-4}	3×10^{-5}	8×10^{-6}
35	1×10^{-1}	1×10^{-3}	8×10^{-4}	4×10^{-5}	2×10^{-6}
40	7×10^{-2}	3×10^{-3}	9×10^{-6}	2×10^{-5}	4×10^{-6}
45	3×10^{-2}	5×10^{-3}	4×10^{-4}	6×10^{-6}	5×10^{-6}
50	6×10^{-2}	1×10^{-3}	6×10^{-5}	9×10^{-6}	3×10^{-6}

Table 3: Relative error in $\tan\delta_0$ for repulsive potential (5.5) with $\lambda=4$ and $k=.5$ atomic units.

$\alpha=1.0$					
M	$N=0$	$N=3$	$N=4$	$N=5$	$N=6$
0	8×10^{-2}	5×10^{-4}	5×10^{-3}	5×10^{-3}	1×10^{-2}
1	5×10^{-3}	3×10^{-4}	5×10^{-3}	7×10^{-3}	2×10^{-3}
2	8×10^{-4}	4×10^{-4}	2×10^{-4}	3×10^{-6}	5×10^{-5}
3	6×10^{-4}	4×10^{-5}	6×10^{-5}	4×10^{-5}	7×10^{-6}
4	1×10^{-4}	1×10^{-5}	2×10^{-6}	6×10^{-8}	1×10^{-8}
5	1×10^{-4}	7×10^{-6}	2×10^{-7}	2×10^{-8}	2×10^{-9}
$\alpha=2.0$					
M	$N=0$	$N=3$	$N=4$	$N=5$	$N=6$
5	1×10^{-3}	6×10^{-4}	3×10^{-5}	7×10^{-5}	1×10^{-6}
6	6×10^{-4}	2×10^{-4}	8×10^{-7}	1×10^{-5}	3×10^{-6}
7	2×10^{-4}	2×10^{-5}	9×10^{-6}	4×10^{-7}	2×10^{-6}
8	4×10^{-4}	1×10^{-5}	6×10^{-6}	5×10^{-7}	1×10^{-6}
9	3×10^{-4}	8×10^{-6}	2×10^{-6}	9×10^{-8}	5×10^{-7}
10	5×10^{-5}	2×10^{-6}	4×10^{-7}	9×10^{-8}	4×10^{-7}

Table 4: Relative error in $\tan \delta_0$ for attractive potential (5.5) with $\lambda = 4$ and $k = .5$ atomic units.

$\alpha = 1.0$					
M	$N = 0$	$N = 3$	$N = 4$	$N = 5$	$N = 6$
5	3×10^{-4}	8×10^{-6}	1×10^{-5}	1×10^{-5}	1×10^{-5}
6	5×10^{-5}	9×10^{-6}	3×10^{-6}	2×10^{-6}	2×10^{-6}
7	1×10^{-4}	3×10^{-6}	3×10^{-9}	2×10^{-7}	2×10^{-7}
8	7×10^{-6}	7×10^{-7}	2×10^{-9}	3×10^{-8}	1×10^{-8}
9	3×10^{-5}	7×10^{-7}	1×10^{-8}	3×10^{-9}	3×10^{-9}
10	1×10^{-5}	3×10^{-7}	2×10^{-8}	2×10^{-9}	2×10^{-9}
$\alpha = 2.0$					
M	$N = 0$	$N = 3$	$N = 4$	$N = 5$	$N = 6$
5	1×10^{-3}	2×10^{-3}	1×10^{-4}	1×10^{-4}	4×10^{-6}
6	2×10^{-3}	8×10^{-4}	3×10^{-5}	3×10^{-5}	9×10^{-7}
7	4×10^{-4}	2×10^{-4}	1×10^{-5}	3×10^{-6}	2×10^{-6}
8	8×10^{-4}	8×10^{-6}	2×10^{-5}	5×10^{-7}	2×10^{-6}
9	9×10^{-4}	3×10^{-5}	8×10^{-6}	3×10^{-7}	1×10^{-6}
10	4×10^{-4}	8×10^{-6}	2×10^{-6}	5×10^{-8}	7×10^{-7}